

SYNTHESIS AND PROPERTIES OF TRANSITION METAL TO CARBON BONDS

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ABSTRACT

The known properties of alkyl and aryl derivatives of transition elements are reviewed, with particular attention to binary compounds of this type. Factors contributing to thermal stability of metal-carbon σ -bonds are discussed and new contributions are presented dealing with: (i) chemistry of titanium(IV) and titanium(II); (ii) metal-carbon bonds in *N,N'*-ethylenebis(salicylideneiminato) complexes of iron and cobalt; (iii) reactivity of rhenium(I) bromo-carbonyl complexes; (iv) use of metal carbonyls as a source of zerovalent metals in the preparations of binary complexes of 9,10-phenanthrenequinone and (v) synthesis of cyclopentadienyl-alkyl and cyclopentadienyl-aryl derivatives of uranium(IV).

INTRODUCTION

In the past decades chemists have lived in the belief that alkyl and aryl derivatives of transition metals had to be unstable. This belief came from the observation that while several organometallic compounds of non-transition elements were known and were thermally stable under ordinary conditions, pure binary compounds of transition elements had been until quite recently a rarity. Some of them have been recently synthesized, however (see *Table 1*). Some examples of non-binary alkyl and aryl derivatives of transition metals are given in *Tables 2* and *3*. Although the *Tables* contain only a limited number of selected examples, some interesting observations can be made.

Table 1. Some binary alkyl derivatives of d-transition elements

| Compound | Colour | m.p. (°C) | Reference |
|---|-------------|--------------------|-----------|
| Ti(CH ₂ C ₆ H ₅) ₄ | red-brown | 70-71 | 1 |
| Zr(CH ₂ C ₆ H ₅) ₄ | yellow | 133-134 | 1 |
| Cr(CH ₂ SiMe ₃) ₄ | dark-purple | 38 | 2a, 2b |
| WMe ₆ | red | c. 30 (dec. 50) | 3 |

(i) Stable organometallic compounds of transition metals exist even with

Table 2. Some non-binary alkyl and aryl compounds of d-transition elements in their highest usual oxidation states

| Compound | Colour | m.p. (°C) | Reference |
|---|------------|--------------|--------------|
| Ti(C ₅ H ₅) ₂ (CH ₂ C ₆ H ₅) ₂ | violet | 109–111 | 4a, 4b |
| Zr(C ₅ H ₅) ₂ (CH ₂ C ₆ H ₅) ₂ | yellow | c. 100 | 5 |
| Zr(C ₅ H ₅) ₂ Me ₂ | — | — | 6 |
| VO(CH ₂ SiMe ₃) ₃ | yellow | 75 | 2 |
| FeSaEn-CH ₂ C ₆ H ₅ † | red | dec. 70 | 7 |
| CoSaEn-Me | red | — | 8, 9, 10, 11 |
| Ni(lipy)Me ₂ | green | — | 12a, 12b |
| Pt(PR ₃) ₂ Me ₄ | colourless | — | 13a |
| Pt(C ₅ H ₅)Me ₃ | colourless | 108.5‡ | 13b |
| Au ₂ Me ₆ (NH ₂ CH ₂ CH ₂ NH ₂) | colourless | dec. 94–98 | 14a |
| Au(PMe ₃)Me ₃ | — | dec. 120 | 14b, 15 |
| Au(PPh ₃)(C ₆ F ₅) ₃ | colourless | dec. 243–246 | 16 |

† FeSaEn stands for : *N,N'*-ethylenebis(salicylideneiminato)iron(II).

‡ At 115°C, about 99 per cent of the substance was recovered unchanged after 75 min.

the metal in its highest usual oxidation state (Ti^{IV}, Zr^{IV}, V^V, W^{VI}, Fe^{III}, Pt^{IV}, Au^{III}).

(ii) Alkyl- and aryl-metal bonds can be stable also when the metal is in an unusually low oxidation state (Mo^{II}, Re^I, Os^{II}, Co^I): this usually happens in connection with cyclopentadienyl and carbon monoxide groups, especially the latter, which are known to stabilize low oxidation states as π -acids.

Before discussing points (i) and (ii) in some detail, it is worthwhile to define what should usually be meant by stability of metal-carbon σ -bonds.

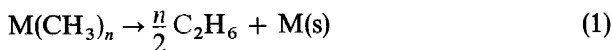
These introductory remarks are essentially restricted to metal-alkyl and metal-aryl σ -bonds, whereas the rest of this article will deal with metal-carbon bonds in general, including two-electron carbon donors, such as carbon monoxide and isocyanides.

Thermodynamic stability should be distinctly separated from kinetic stability, of course. Unfortunately, sufficient data are not yet available to discuss thermodynamic stability properly. It seems, however, from the few data available (see Table 4) that metal-carbon σ -bonds to titanium and platinum are not inherently weak, since the estimated values for the mean dissociation energies range from 60 to 84 kcal mol⁻¹. This does not necessarily mean that the observed thermal stability of some metal-carbon bonds to

Table 3. Some non-binary alkyl compounds of d-transition elements in low oxidation states

| Compound | Colour | m.p. (°C) | Reference |
|--|------------|-----------|-----------|
| Cr(C ₅ H ₅)(CO) ₃ Me | yellow | — | 17 |
| Cr(C ₆ H ₂ Me ₃) ₂ · 3THF | violet | dec. 50 | 18 |
| Mo(C ₅ H ₅)(CO) ₃ Et | yellow | 77–78 | 17 |
| Mn(CO) ₅ Me | colourless | 94.5–95 | 19 |
| Re(CO) ₅ Me | colourless | 120 | 20 |
| Os(CO) ₄ Me ₂ | colourless | — | 21, 22 |
| Co(CO) ₄ Me | yellow | -44 | 23 |

transition metals is thermodynamic. In fact, it is highly probable that most or all of the compounds containing, for example, metal–methyl bonds would be thermodynamically unstable with respect to the homolytic fission:



Most of the compounds reported in *Tables 1* and *2* have been prepared quite recently. While some years ago it appeared necessary to find an explanation for the stabilizing effect of ligands such as carbon monoxide and tertiary phosphines, the inherent instability of metal–carbon bonds being taken for granted, today it is important to interpret correctly the experimental observation that some binary metal–alkyl compounds can be isolated and handled under normal operative conditions.

The situation could therefore be stated in the following terms. The problem concerning the existence of thermally-stable transition-element–carbon bonds is less intriguing now than it was some years ago. However, the thermal stability, which is controlled almost certainly by kinetic factors, has still to be explained. The main factors which have been or may be considered in order to explain the scarce availability of low-energy paths for the breaking of metal–carbon σ -bonds are: (i) stabilization of metal–carbon bonds with respect to olefin elimination^{2b, 3}; (ii) the electronic configuration and the

Table 4. Calorimetric mean bond dissociation energies (MBDE) of some metal–carbon bonds

| Metal–C bond | Compound | MBDE (kcal mol ⁻¹) | Reference |
|--------------|---|-----------------------------------|-----------|
| Ti–Me | Ti(C ₅ H ₅) ₂ Me ₂ | 60 | 24 |
| Ti–Ph | Ti(C ₅ H ₅) ₂ Ph ₂ | 84 | 24 |
| Pt–Ph | Pt(PEt ₃) ₂ Ph ₂ | 60 | 25 |
| Hg–Me | HgMe ₂ | 29 | 26 |

symmetry of the central metal atom, which in some cases can prevent the mixing of ground and excited vibrational states²⁷; (iii) the promotion of electrons to excited states²⁸, which may explain the photochemical lability of surprisingly stable metal–carbon bonds of some cobalt(III) derivatives^{8–11}; (iv) the absence of vacant coordination positions and (v) a relatively high oxidation state for the central metal atom.

Point (v) originates from the data of *Tables 1* and *2* and may be related, in classical terms, to an increased stability of the carbanion bonded to the metal. Of course, it is very likely that none of the above mentioned factors alone will explain all the known facts.

That the metal has to be saturated from a coordinative point of view (this may be either a kinetic or a thermodynamic stabilization) should be an important fact.

It is interesting to note that tetrabenzyltitanium(IV) has an intense red-brown colour, which is certainly not to be attributed to a $d \rightarrow d$ transition in view of the high intensity and, of course, to the fact that we are dealing with a

d^0 -system. The intensity of the absorption is in favour of a charge-transfer type of transition. It is interesting to observe that the x-ray structure of this compound^{29, 30} has clearly shown that, in spite of the fact that there is not a π -allyl type of stabilization to be invoked, involving two of the aromatic ring carbon atoms, the conformation of the molecule is such that a considerable interaction may be suggested between the central metal atom and at least one of the aromatic groups. As it can be seen in *Figure 1*, one of the four Ti-C-C

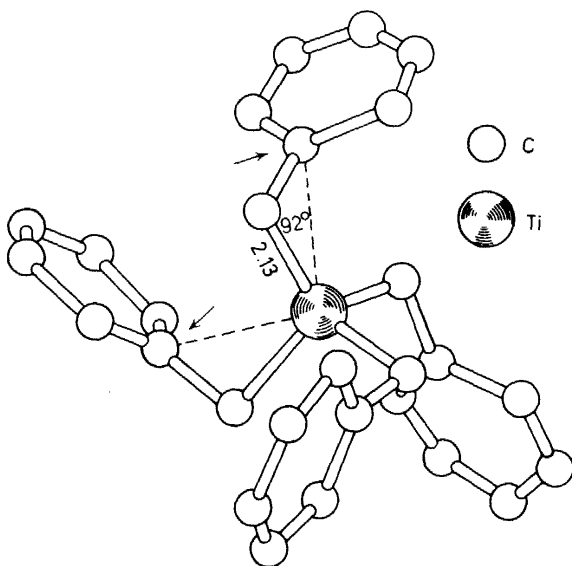


Figure 1. Molecular structure of $\text{Ti}(\text{CH}_2\text{C}_6\text{H}_5)_4$ showing that the angle at one of the four methylene groups is 92° . From G. R. Davies, J. A. J. Jarvis and B. T. Kilbourn, *Chem. Commun.*, 1511 (1971). See also Ref. 29

angles at the methylene group is 92° . The other such angles are 98° , 109° and 115° , two of them, therefore, being much smaller than expected. An interaction between empty d-orbitals of the metals and p-orbitals of the aromatic rings was therefore suggested^{29, 30}. It is possible that this interaction may at least in part be responsible for both the stability (occupation of coordination sites) and the colour of the complex. In the similar zirconium compound³¹, $\text{Zr}(\text{CH}_2\text{C}_6\text{H}_5)_4$, the angles at the methylene groups are 85° , 90° , 92° and 101° , i.e. even smaller than for the titanium compound.

In connection with colour, it should be mentioned that the reported³ red colour of hexamethyltungsten(vi) is intriguing since it is not obvious which orbitals are involved in the electronic transitions occurring at such low energy.

We can now consider some of the experimental results that have been recently obtained in our and other laboratories. Some of these results may be helpful towards a better understanding of the problem connected with the stability of metal-carbon σ -bonds. The metals at the beginning (titanium

and zirconium) and in the middle (rhenium) of the transition d-series have been chosen and examples will also be presented of stable uranium-carbon σ -bonds. Also, results concerning some properties of cobalt and iron organo-metallic compounds in macrocyclic molecules will be discussed since this will raise some interesting points connected with the stability of metal-carbon σ -bonds discussed above.

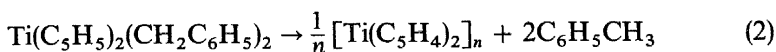
TITANIUM AND ZIRCONIUM

The chemical properties of the tetrabenzyl derivatives of titanium and zirconium have been extensively studied by Giannini and co-workers¹. They have indicated that the titanium derivative undergoes reduction to titanium(III) in solution, accompanied by formation of toluene. This is suggestive of a concerted homolytic cleavage and hydrogen abstraction, the latter being most probably intramolecular (see below). In fact, by working with deuterated solvents, it was possible to show that the solvent was not involved in the formation of toluene.

Our results³², together with those reported by Giannini and co-workers, suggest that tetrabenzyltitanium(IV) is very reactive towards either electrophilic reagents, such as alcohols and hydrogen halides, to give toluene, or nucleophilic reagents such as carbon monoxide and isocyanides. The former reactivity is most probably related with an attack at the benzyl carbon atom, whereas the latter may have something to do with an associative type of attack at the metal. Despite its considerable thermal stability, tetrabenzyltitanium is very reactive towards carbon monoxide. We have studied this reaction as a possible method for preparing a still unknown binary carbonyl of titanium, via the reductive homolytic fission of the metal-carbon bond. The products of the reaction with carbon monoxide are very complicated and they are still under investigation³².

It is interesting to note that the metal-aromatic ring interactions which have been discussed earlier in connection with the molecular structures of $\text{Ti}(\text{CH}_2\text{C}_6\text{H}_5)_4$ and $\text{Zr}(\text{CH}_2\text{C}_6\text{H}_5)_4$ may be responsible for the considerable upfield shift of the *ortho*-aromatic protons observed by different authors^{1, 33}. In agreement with this, is the fact that the ¹H n.m.r. spectra of the corresponding bis(cyclopentadienyl) derivatives, $\text{Ti}(\text{C}_5\text{H}_5)_2(\text{CH}_2\text{C}_6\text{H}_5)_2$ and $\text{Zr}(\text{C}_5\text{H}_5)_2(\text{CH}_2\text{C}_6\text{H}_5)_2$ show⁵ a multiple pattern typical of phenyl protons. Of course, steric hindrance is more important for these cyclopentadienyl derivatives and the electronic demand by the central metal atom is less stringent.

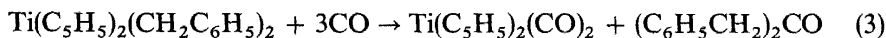
The bis(cyclopentadienyl)dibenzyl derivatives of titanium(IV) and zirconium(IV) present largely different thermal stabilities and chemical reactivities⁵. While the zirconium compound can be recrystallized from boiling heptane, the titanium analogue, $\text{Ti}(\text{C}_5\text{H}_5)_2(\text{CH}_2\text{C}_6\text{H}_5)_2$, decomposes in benzene solution at about 30°C, according to the following stoichiometry:



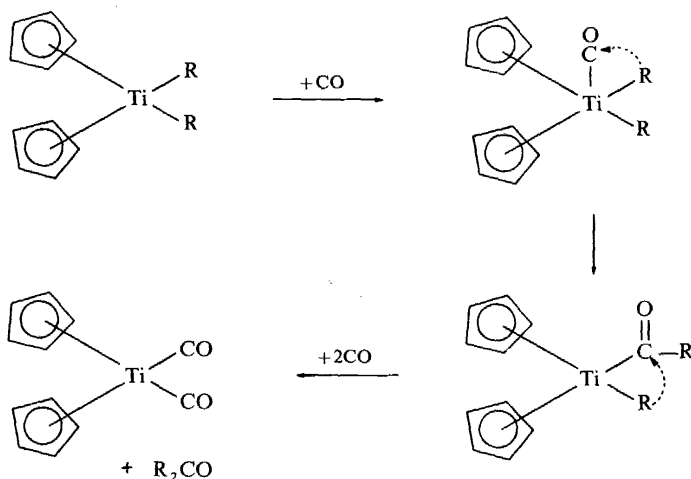
The titanium compound resulting from reaction (2) is a black solid, whose structure is still under investigation. It has been established that toluene was

not formed by hydrogen abstraction from the solvent. This is another case of intramolecular hydrogen abstraction from bonded-cyclopentadienyl groups: several other examples of the same type have been reported recently³⁴⁻³⁶, and another one will be reported in a later section of this article.

Bis(cyclopentadienyl)dibenzyltitanium(IV) undergoes a reaction with carbon monoxide under mild conditions⁵, similar to $\text{Ti}(\text{CH}_2\text{C}_6\text{H}_5)_4$; in this case, however, well-defined products were obtained. The reaction occurs according to the following stoichiometry:



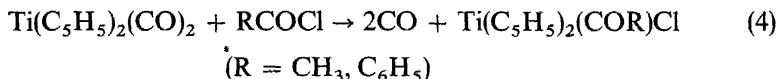
The carbonylation reaction can be visualized to occur (*Scheme 1*) via a pre-coordination of CO to titanium, followed by alkyl migrations and formation of the final dicarbonyl, $\text{Ti}(\text{C}_5\text{H}_5)_2(\text{CO})_2$.



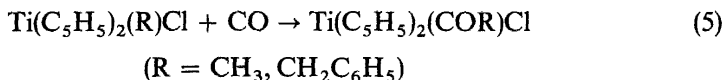
Scheme 1. Carbonylation of bis(cyclopentadienyl)dibenzyltitanium (IV)

This mechanism involves an alkyl migration step, similar to that which has been suggested to occur in carbonylation reactions of $\text{CH}_3\text{Mn}(\text{CO})_5$ ^{37, 38}.

An important step towards the credibility of *Scheme 1* was made by Floriani and Fachinetti with the synthesis of acyl derivatives of titanium(IV). These compounds were prepared either by the reaction of $\text{Ti}(\text{C}_5\text{H}_5)_2(\text{CO})_2$ with acyl chloride³⁹:



or by carbonylation of $\text{Ti}(\text{C}_5\text{H}_5)_2(\text{CH}_3)\text{Cl}$ and $\text{Ti}(\text{C}_5\text{H}_5)_2(\text{CH}_2\text{C}_6\text{H}_5)\text{Cl}$ with carbon monoxide⁴⁰:



Reactions (4) and (5) have some interesting features.

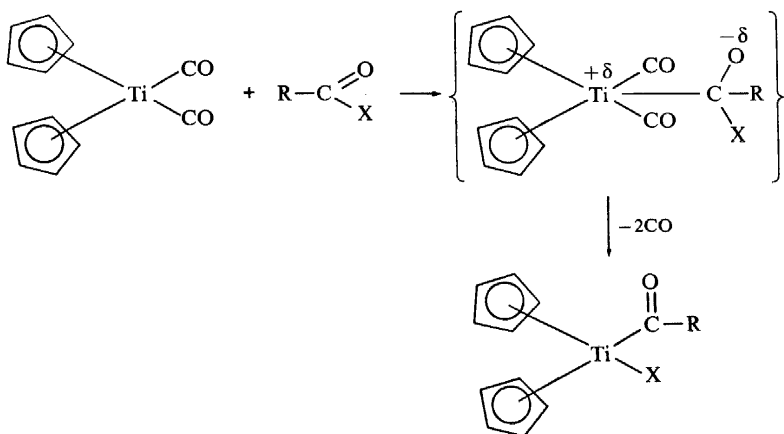
(i) They yielded the first acyl derivatives of titanium reported in the literature. These compounds are, as expected, characterized by a carbonyl C—O stretching vibration around 1600 cm^{-1} which shifts slightly depending on the group R (see Table 5). It is interesting to note that insertion reactions of alkyl and aryl derivatives of titanium(IV) and zirconium(IV) with SO_2 and NO have been recently described^{41, 42}.

Table 5. Infrared and ^1H n.m.r. data for acyl derivatives of titanium(IV) of formula $\text{Ti}(\text{C}_5\text{H}_5)_2\text{COR}(\text{X})$

| R | X | $\nu_{\text{C-O}}(\text{cm}^{-1})$ | ^1H n.m.r. data† | | |
|-----------------------------------|--------|------------------------------------|-------------------------------|--------------|------------------------|
| | | | Chemical shift (ppm, τ) | Multiplicity | Assignment |
| CH_3 | Cl(I) | 1620 | 4.2 | singlet | C_5H_5 |
| | | | 7.0 | singlet | CH_3 |
| CH_3 | I(II) | 1610 | 4.2 | singlet | C_5H_5 |
| | | | 7.0 | singlet | CH_3 |
| C_2H_5 | I(III) | 1605 | 4.2 | singlet | C_5H_5 |
| | | | 6.7 | quadruplet | CH_2 |
| | | | 8.6 | triplet | CH_3 |
| C_6H_5 | Cl(IV) | 1600 | 1.9 | singlet | C_6H_5 |
| | | | 3.9 | singlet | C_5H_5 |
| $\text{C}_6\text{H}_5\text{CH}_2$ | Cl(V) | 1625 | 2.7 | singlet | C_6H_5 |
| | | | 4.3 | singlet | C_5H_5 |
| | | | 5.5 | singlet | CH_2 |

† Data from References 39 and 40.

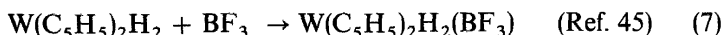
(ii) Reaction (4) can be classified as an oxidative-addition reaction⁴³, although no expansion of the coordination sphere of the metal occurs. Mechanistically it is believed that the addition of acyl halide to $\text{Ti}(\text{C}_5\text{H}_5)_2(\text{CO})_2$ takes place by a nucleophilic type of attack of the metal complex on the acyl carbon, as indicated in Scheme 2.



Scheme 2. Oxidative-addition of acyl halide to $\text{Ti}(\text{C}_5\text{H}_5)_2\text{CO}_2$

The nucleophilic character of $\text{Ti}(\text{C}_5\text{H}_5)_2(\text{CO})_2$ is suggested by the basic properties shown by similar d^2 -systems having bent cyclopentadienyl structures, such as, for example, $\text{Mo}(\text{C}_5\text{H}_5)_2\text{H}_2$ and $\text{W}(\text{C}_5\text{H}_5)_2\text{H}_2$.

The following reactions are known, for example:



Attempts to rationalize the basic properties of bent bis(cyclopentadienyl) systems have been made by Balhausen and Dahl⁴⁶, by Alcock⁴⁷ and, more recently, by Prout and co-workers⁴⁸. The essential features of the bonding scheme proposed are schematically shown in *Figure 2*. The main concern is about the location of the essentially non-bonding orbital which should account for the basic properties of d^2 -systems of this type.

The presence of electrons in an essentially non-bonding orbital of $\text{Ti}(\text{C}_5\text{H}_5)_2(\text{CO})_2$, capable, at least in principle, of π -bonding with empty orbitals on carbon monoxide, is substantiated by the strikingly low wave-number values for the carbonyl stretching vibrations (1975 and 1897 cm^{-1} in heptane) which had been noticed earlier⁴⁹.

Some oxidative-addition reactions on the so-called titanocene dimer had been reported earlier^{50, 51}. Some of them were *only partially* successful⁵¹ and it is also interesting to note that the reaction⁵² of hydrogen chloride to the titanocene dimer does not yield the expected product for the oxidative-addition, i.e. $\text{Ti}(\text{C}_5\text{H}_5)_2(\text{H})\text{Cl}$, but rather a presumed chlorine-bridged dimer³⁴ of formula $(\text{TiClC}_{10}\text{H}_9)_2$. This anomalous behaviour is believed^{39, 40} to be due to the fact that the titanocene dimer cannot be regarded, because of its probable molecular structure, as a source of monomeric titanocene, $\{\text{Ti}(\text{C}_5\text{H}_5)_2\}$. The titanocene dimer has now been established definitely to be a hydride species of formula $[\text{Ti}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4)\text{H}]_2$, although no complete agreement about its structure seems to have been found as yet. Structures have been proposed for the dimer, with bridging³⁴ and with terminal⁵³ hydrido ligands. *Figures 3* and *4* show schematically the proposed structures for the titanocene dimer and the molecular structure of the niobocene dimer⁵³, respectively. The latter compound has terminal hydrido groups and the suggestion was made⁵³ that the titanocene dimer would have a similar arrangement with bridging C_5H_4 units.

The acyl derivatives (II) and (IV) of *Table 5* were obtained^{39, 40} by the

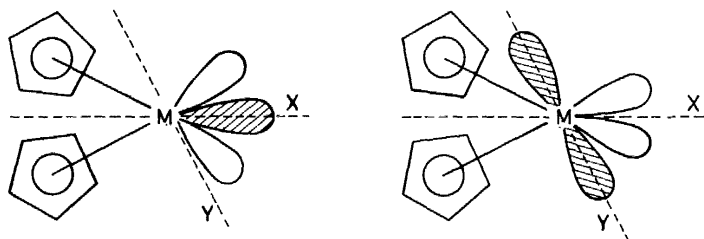
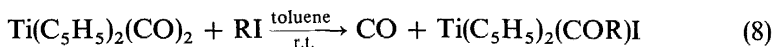


Figure 2. The location of the essentially non-bonding orbital (shaded) in d^2 -systems of the type $\text{Ti}(\text{C}_5\text{H}_5)_2\text{X}_2$, according to Balhausen and Dahl⁴⁶ (left) and according to Alcock⁴⁷. For a discussion of the bonding see also Prout and co-workers⁴⁸

SYNTHESIS AND PROPERTIES OF TRANSITION METAL TO CARBON BONDS
 oxidative-additions to $\text{Ti}(\text{C}_5\text{H}_5)_2(\text{CO})_2$ of methyl and ethyl iodide, respectively:



Other oxidative-addition reactions reported^{39, 40} were:

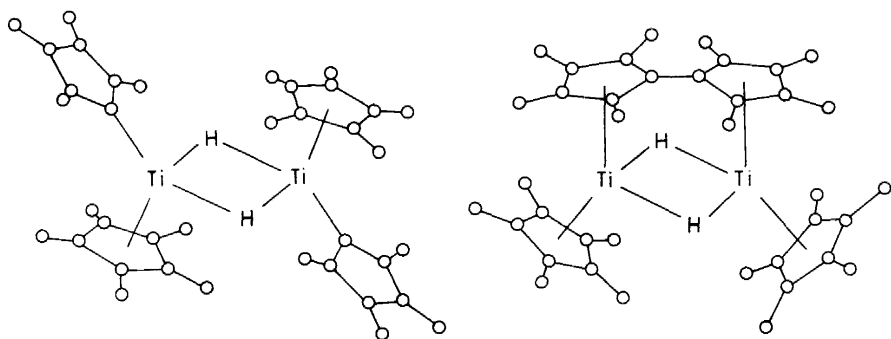
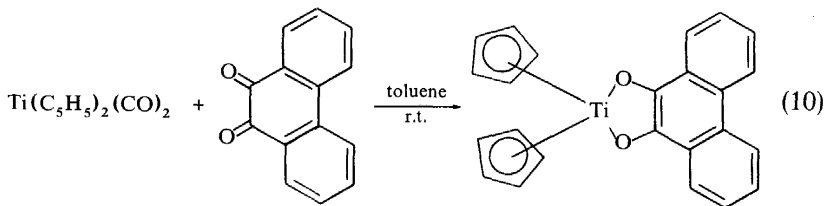
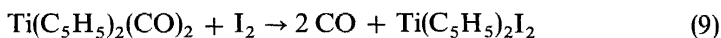


Figure 3. Proposed structures of the titanocene dimer. From H. H. Brintzinger and J. E. Bercaw, *J. Am. Chem. Soc.*, **92**, 6182 (1970)

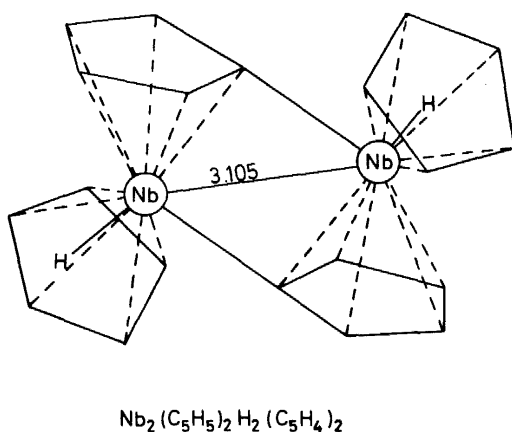
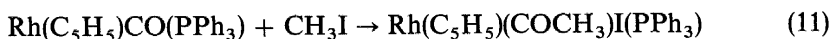


Figure 4. The molecular structure of the niobocene dimer schematically drawn. From L. J. Guggenberger and F. N. Tebbe, *J. Am. Chem. Soc.*, **93**, 5924 (1971)

Reaction (8) is similar to that observed recently⁵⁴ between $\text{Rh}(\text{C}_5\text{H}_5)\text{CO}(\text{PPh}_3)$ and CH_3I :

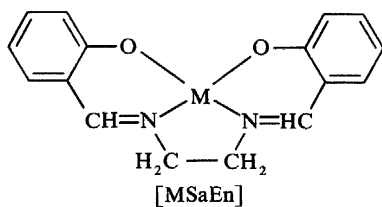


It is worth mentioning that the acyl titanium(IV) derivatives recently prepared contain the highest oxidation state known, at the present time, in organometallic acyl compounds. Their stability may appear somewhat surprising. It may be suggested that the acyl derivatives may gain some stability from overlapping between filled orbitals of the acyl group and empty orbitals of titanium. This interaction, which has to be intramolecular because the compounds were found³⁹ to be monomeric in CHCl_3 , may explain the considerably low wavenumber values for the carbonyl C—O stretching vibration (see Table 5). This would be a stabilization similar to the so-called β -effect⁵⁵; the electronic situation would be favourable in this case in view of the considerable extension in space of d-orbitals⁵⁶ at the beginning of a transition series with respect to elements of higher atomic number.

As a conclusion of this section on organometallic compounds of titanium, i.e. an early element of the 3d-transition series, it may be said that the stabilization of metal-carbon bonds by the benzyl group in d^0 -systems may be attributed to stabilization of the carbanion through the aromatic unsaturation, interaction of the metal orbitals with the aromatic ring, and difficult olefin elimination. The carbonylation of $\text{Ti}(\text{C}_5\text{H}_5)_2\text{R}_2$ and $\text{Ti}(\text{C}_5\text{H}_5)_2(\text{R})\text{Cl}$ may provide a good model for the catalytic polymerization. The latter compound was proposed^{56a} to be the true catalyst for the olefin polymerization. Also, a drastic change of reactivity has been shown to take place on going from titanium(IV) to titanium(II) organometallic compounds. Whereas the former will tend to undergo either nucleophilic attack at the metal (as shown by the reactions of $\text{Ti}(\text{CH}_2\text{C}_6\text{H}_5)_4$ with CO) or electrophilic attack at the carbon atom (reaction of $\text{Ti}(\text{CH}_2\text{C}_6\text{H}_5)_4$ with proton active substances), the titanium(II) derivatives will preferentially behave as nucleophiles towards RCOX , RX and halogens.

METAL-CARBON BONDS IN MACROCYCLIC COMPLEXES WITH DELOCALIZED UNSATURATION

A few years ago we became interested in the chemical and physical properties of some Schiff's base metal complexes. In particular we have studied the N,N' -ethylenebis(salicylideneiminato) metal complexes (see below), for which we shall be using the abbreviation MSaEn throughout.



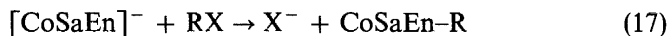
Our interest in this type of complex began in 1965 with the aim of studying the chemical^{57, 58} and magnetic properties⁵⁸ of CoSaEn-oxygen adducts. More recently our attention has been directed towards chemical reductions of these systems and formation of metal-carbon σ -bonds.

We have found that several metal-SaEn systems can be reduced by sodium in tetrahydrofuran, yielding the reduced species resulting from one-electron and two-electron additions^{9, 11, 59}. The following reactions were successfully carried out:



The existence of the $[\text{CoSaEn}]^{2-}$ anion was later confirmed by Vol'pin and co-workers⁶⁰ who carried out the electron transfer reaction to cyclo-octatetraene, yielding $\text{C}_8\text{H}_8^{2-}$ and $[\text{CoSaEn}]^-$.

The most interesting properties of the reduced species are: (i) the bulk magnetic susceptibility and (ii) the chemical reactivity, especially towards electrophilic reagents such as alkyl and acyl halides. As far as magnetic susceptibility data are concerned, $[\text{FeSaEn}]^-$ and $[\text{CoSaEn}]^-$ can be regarded as d^7 - and d^8 -systems of high-spin and low-spin behaviour, respectively. In view, in particular, of the result obtained with the cobalt compound⁶¹, it was to be expected that this presumably square complex of d^8 -configuration would undergo the oxidative-addition reactions, typical of these systems⁴³. The assumption of a square or nearly-square arrangement for the $[\text{CoSaEn}]^-$ anion, besides other evidence, is based on the results of a recent x-ray investigation of the pentacoordinate pyridine adduct, $\text{CoSaEn} \cdot \text{C}_5\text{H}_5\text{N}^{61a}$. It has been shown that the N_2O_2 donor atoms of the Schiff's base are coplanar, although the cobalt atom is out of the N_2O_2 plane by 0.20 Å. An even more regular structure is expected for $[\text{CoSaEn}]^-$, due to the absence of axial ligand. In conformity with the expectations mentioned above, it has been found that the $[\text{CoSaEn}]^-$ anion behaves as a strong nucleophile and reacts^{9, 11} rapidly, even at temperatures as low as -80°C with alkyl and acyl halide:



The reduction of CoSaEn to $[\text{CoSaEn}]^-$ and the conversion of the latter to alkyl and acyl derivatives of cobalt (III) was found independently also by Costa and his co-workers⁸.

It is conceivable that the formation of the organometallic derivative is the result of an oxidative-addition of RX to $[\text{CoSaEn}]^-$, to give an anionic organometallic derivative of cobalt(III), followed by X^- elimination:



The x-ray structures of some CoSaEn-alkyl derivatives have been reported. The ethyl derivative is an oxygen-bridged dimer⁶², $[\text{CoSaEn}-\text{C}_2\text{H}_5]_2$. The cyanomethylene derivative, $\text{CoSaEn}-\text{CH}_2\text{CN} \cdot \text{CH}_3\text{OH}$, has a polymeric structure⁶³ through nitrogen-bridging cyanomethylene groups; the acetyl derivative, $\text{CoSaEn}-\text{CH}_2\text{COCH}_3 \cdot \text{CH}_3\text{OH}$, has intermolecular hydrogen bonds⁶³. The molecular structure of the cyanomethylene cobalt (III) compound is schematically drawn in *Figure 5*. It is interesting to note that cyanomethylene and the acetyl compounds were obtained⁶⁴ from CH_3CN and CH_3COCH_3 and CoSaEn, in the presence of oxygen, in methanol as solvent. These results are in agreement with an observation which was made by us independently some years ago: in the course of the reaction of CoSaEn with CH_3NO_2 in the presence of air, the diamagnetic nitromethylene compound, $\text{CoSaEn}-\text{CH}_2\text{NO}_2$, was obtained.

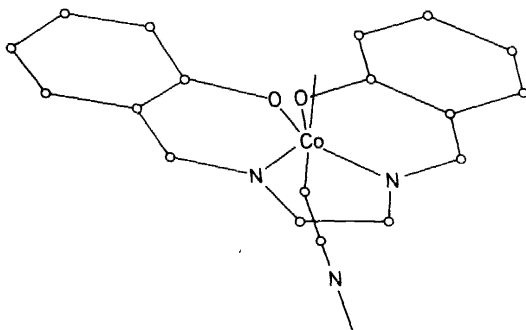


Figure 5. Schematic representation of $\text{CoSaEn}-\text{CH}_2\text{CN} \cdot \text{CH}_3\text{OH}$. The methanol group is not shown for clarity. From M. Cesari, C. Neri, G. Perego, E. Perrotti and A. Zazzetta, *Chem. Commun.*, 276 (1970)

In connection with metal-carbon σ -bonds in these macrocyclic inorganic molecules, it is worth mentioning that some years ago we presented what we believe to be relevant experimental evidence concerning the polarity of the cobalt-carbon bond. We measured¹¹ the ^{59}Co n.m.r. spectrum of some of these compounds and compared the values obtained with those typical of cobalt (III) coordination compounds. The data are reported in *Table 6*. The resonances for the methyl and acetyl derivatives, $\text{CoSaEn}-\text{CH}_3$ and

Table 6. ^{59}Co nuclear magnetic resonance of CoSaEn derivatives†‡

| Compound | Chemical shift§ (ppm) | Line width (gauss) |
|---|--------------------------|-----------------------|
| $\text{CoSaEn}-\text{Br}(\text{PPh}_3)$ | -7510 ± 150 | 50 |
| $\text{CoSaEn}-\text{CH}_3$ | -7125 ± 15 | 6 |
| $\text{CoSaEn}-\text{COCH}_3$ | -6400 ± 10 | 6 |

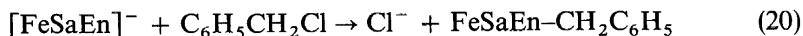
† Data from Reference 11.

‡ Dimethylformamide solutions approximately 0.15M.

§ From aqueous solution of $\text{K}_3[\text{Co}(\text{CN})_6]$.

CoSaEn-COCH₃, respectively, are within the range typical for cobalt (III) coordination compounds and very close to CoSaEn-Br(PPh₃), for which a cobalt(III) formulation is, of course, the most appropriate.

More recently, our interest in this field has been devoted to the study of FeSaEn and TiSaEn systems. Similar to [CoSaEn]⁻, the [FeSaEn]⁻ anion undergoes reactions with alkyl halides to give organometallic derivatives of iron(III). In the case of benzyl chloride, *N,N'*-ethylenebis(salicylideiminato)-benzyliron(III) was isolated in a pure state⁷:



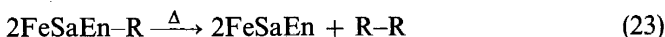
By a different route, the phenyliron (III) compound was also prepared:



The benzyl and phenyl derivatives are red and red-violet solids, respectively, and are sensitive to oxygen. The phenyl derivative reacts with oxygen according to the following stoichiometry:



Both of these organometallic compounds are thermally moderately stable, decomposing at about 60°C to give homolytic iron-carbon bond fission:



It is quite important to realize, in connection with the previous discussion concerning the appearance of high oxidation states for alkyl and aryl derivatives of transition elements, that FeSaEn-R is one of the very few examples reported in the literature of organometallic derivatives of iron(III). Several alkyl and aryl compounds of iron in oxidation state (II) and lower, containing additional ligands such as nitrogen oxide, carbon monoxide, cyclopentadienyl, 2,2'-dipyridyl, and PR₃, are known⁶⁵⁻⁶⁸. However, iron(III) is known, to the best of our knowledge, to bond to carbon via σ-bonds only in an Aetioporphyrin type of structure⁶⁹. Iron(III) organometallic compounds of formula FeSaEn-CH(CN)₂ have been reported at this Conference by McKenzie and co-workers^{69a}. Moreover, it has recently been reported⁷⁰

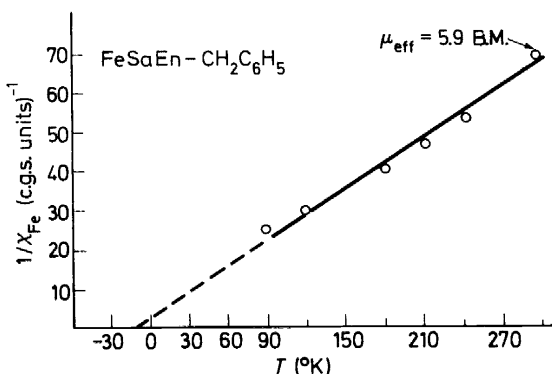


Figure 6. Temperature dependence of magnetic susceptibility for FeSaEn-CH₂C₆H₅

that iron(III) alkyl derivatives are probably intermediates of the reaction between Fe_2Cl_6 and alkyllithium, but no compounds could be isolated.

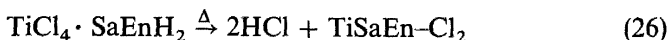
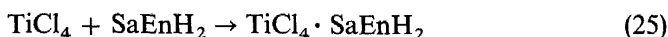
The work with the FeSaEn- and Aetioporphyrin-iron derivatives has shown that iron-carbon σ -bonds may be stable even at this relatively high oxidation state. Even more unusual, however, is the fact that, according to magnetic susceptibility measurements, the benzyl derivative, FeSaEn- $\text{CH}_2\text{C}_6\text{H}_5$, is high-spin⁷. The dependence of molar magnetic susceptibility on temperature is shown in *Figure 6*. The magnetic moment at room temperature is very close to the theoretical spin-only value. This is, of course, quite normal for iron(III) compounds in general since for high-spin d^5 -configurations no orbital contribution to the magnetic moment is expected. On the other hand, the high-spin behaviour is quite unexpected in organometallic chemistry, since no compounds (except for a series of bis(aryl)-chromium(II) of d^4 -configuration, reported some years ago by Stolze and Hähle¹⁸) containing metal-alkyl or metal-aryl σ -bonds have been reported to be high-spin as yet. It is important to realize that, in spite of the population of high-energy states indicated by the magnetic susceptibility measurements, the benzyl derivative (and most probably the phenyl derivative also) is quite stable at room temperature, provided that light is excluded. This experimental evidence should be compared with the Chatt and Shaw theory²⁸ concerning stabilities of metal-carbon σ -bonds. The new findings^{7, 18} suggest that, contrary to what might have been an earlier belief, high-spin behaviour and metal-carbon σ -bonds may coexist. The decomposition of FeSaEn-R compounds, which appears to take place exclusively by metal-carbon fission, may be somewhat prevented by the Schiff's base chelate structure, which tends to minimize intermolecular collisions, yielding the coupling products R-R.

The iron(II) chelate reacts⁷ promptly at room temperature with cyclohexyl isocyanide to give the 1:1 adduct:



The cyclohexyl isocyanide adduct has an absorption band at 2180 cm^{-1} which is attributed to the CN stretching vibration of the coordinated isocyanide group. The magnetic properties of FeSaEn-CNC₆H₁₁ show that the d^6 -iron(II) centre has maintained its high-spin behaviour and the complex still behaves as a normal paramagnetic substance with a magnetic moment, at room temperature, substantially identical with the theoretical spin-only value (*Figure 7*).

We have extended our interest in salicylideneiminato-metal complexes and studied the titanium system. We prepared TiSaEn-Cl₂ by the reaction of TiCl₄ with the Schiff's base:



Bis(salicylideneiminato)dichlorotitanium(IV), obtained by reactions (25)-(26), was also reported by Biradar and Kulkarni⁷¹. The compound is assumed to have an octahedral structure with the two chlorine atoms in *trans* position with respect to the plane containing the N₂O₂ donor atoms of the Schiff's base ligand.

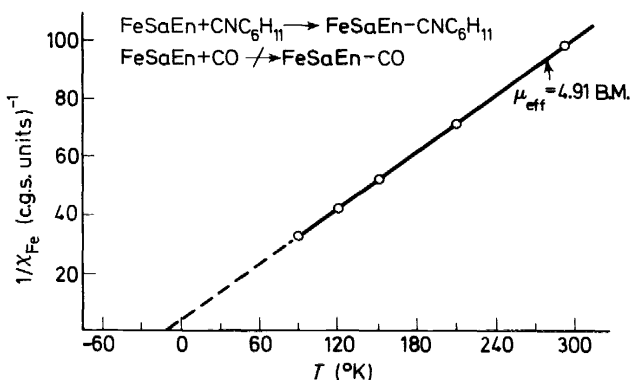


Figure 7. Temperature dependence of magnetic susceptibility for FeSaEn-CNC₆H₁₁

We are presently engaged in a research programme dealing with meta-thetical reactions and reductions of TiSaEn-Cl₂ and we hope to report the results of our investigations in the near future.

ORGANOMETALLIC DERIVATIVES OF GROUP VII TRANSITION ELEMENTS

A considerable amount of work was done in recent years by our research group and others^{37, 38, 72} aimed at clarifying the mechanism of the so-called carbon monoxide insertion reaction in alkyl manganese pentacarbonyls, promoted by a Lewis base L (L = CO, RNH₂, PR₃, I⁻):

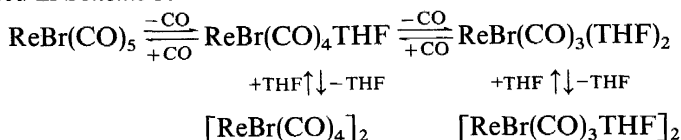


An important feature of the mechanism which has been proposed³⁸ is that two *cis* positions of the coordination sphere of the metal have to be involved in the carbonylation process. This is an important point when dealing with inorganic reaction mechanisms in general and with catalysis in particular.

We are now planning to extend our previous work with carbonylation of alkyl manganese pentacarbonyls to the corresponding rhenium compounds. We believe that this type of 'across-the-group' comparisons of reactivity are quite important. The origin of our interest in this subject was the observation^{73, 74} that sometimes organometallic derivatives in low oxidation state show a maximum of reactivity for the 4d-element.

We therefore attempted to collect some more quantitative data concerning reactions of similar compounds containing metals of the same vertical triad. In the course of such an investigation, while studying the reductions of halogeno-carbonyl derivatives of rhenium(I), we have observed some unexpectedly facile bridge-splitting and substitution reactions. Contrary to earlier reports⁷⁵, and consistent^{75a} with a similar bridge-splitting reaction with [RuCl₂(CO)₃]₂, we have found that both ReBr(CO)₅ and [ReBr(CO)₄]₂ react at room temperature (better at reflux temperature) with tetrahydro-

furan, finally yielding the already known⁷⁵ tricarbonyl derivative $[\text{ReBr}(\text{CO})_3\text{THF}]_2$. The dimer is the species which can be isolated from the solution, but there is infrared evidence⁷⁶ that in solution the tricarbonyl compound is present as the solvated species $\text{ReBr}(\text{CO})_3(\text{THF})_2$. The same is most probably true for the tetracarbonylbromorhenium(i) compound, which is a dimer⁷⁷ in solution of presumably non-coordinating solvents. The dimeric tetracarbonylbromo complex is now suggested to be converted rapidly by tetrahydrofuran into the monomeric solvated species. These conclusions originate from the infrared study⁷⁶ of bromocarbonyls of rhenium(i) in different solvents. The situation concerning these compounds is indicated in *Scheme 3*.



Scheme 3. Reactions of bromocarbonyls of rhenium(i) in tetrahydrofuran

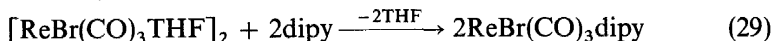
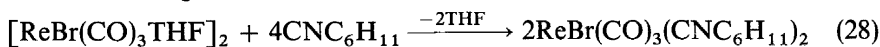
The infrared data concerning the pentacarbonyl-, tetracarbonyl- and tricarbonylbromorhenium(i) species are reported in *Table 7*. It will be noticed that the spectra in tetrahydrofuran of $[\text{ReBr}(\text{CO})_4]_2$ and $[\text{ReBr}(\text{CO})_3\text{THF}]_2$ are different from those of the same substances in other solvents with less or no coordinating power. The differences are so large that this cannot be attributed to just a solvent effect. Moreover, the spectrum of $[\text{ReBr}(\text{CO})_4]_2$ is

Table 7. Infrared carbonyl and C—N stretchings of some bromocarbonyls of rhenium(i)

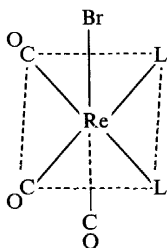
| Compound | Solvent | $\nu_{\text{C-N}}(\text{cm}^{-1})$ | | $\nu_{\text{C-O}}(\text{cm}^{-1})$ | | |
|---|-----------------|------------------------------------|-------|------------------------------------|---------|---------|
| $\text{ReBr}(\text{CO})_5$ | CCl_4 | — | 2153w | 2045s | 2016w | 1982m |
| | CHCl_3 | | 2154w | 2047s | 2020w | 1987m |
| | THF | | 2152w | 2040s | 2020w | 1981m |
| $[\text{ReBr}(\text{CO})_4]_2$ | CHCl_3 | — | 2114w | 2035s | 2000m | 1960m |
| | THF | | 2113w | 2009s | 1984m | 1931m-s |
| $[\text{ReBr}(\text{CO})_3\text{THF}]_2$ | heptane | — | 2036m | | 1928s | |
| | benzene | | 2032m | | 1921s | |
| | CHCl_3 | | 2032m | | 1924s | |
| | THF | | 2030m | | 1914s | 1891s-m |
| $\text{ReBr}(\text{CO})_3(\text{CNC}_6\text{H}_{11})_2$ | CHCl_3 | 2207m | 2181m | 2040s | 1980s-m | 1920s |
| | THF | 2205m | 2180m | 2034s | 1972s-m | 1918s-m |
| $\text{ReBr}(\text{CO})_3(\text{dipy})$ | CHCl_3 | — | | 2025s | 1925m-s | 1898m-s |
| | THF | | | 2020s | 1918m-s | 1894m-s |

similar to those of tetracarbonyl-substituted compounds of formula $\text{ReBr}(\text{CO})_4\text{L}^{77a}$ (for example, $\text{ReBr}(\text{CO})_4\text{py}$ was reported to have the following bands in tetrachloroethane: 2113m, 2012vs, 1996sh, 1932s cm^{-1}) and the spectrum of $[\text{ReBr}(\text{CO})_3\text{THF}]_2$ in tetrahydrofuran is very similar to that of $\text{ReBr}(\text{CO})_3\text{dipy}$ (see *Table 7*). It is thus possible to conclude that the dimeric compounds undergo fast bridge-splitting reactions in tetrahydrofuran.

The following reactions were also carried out successfully:



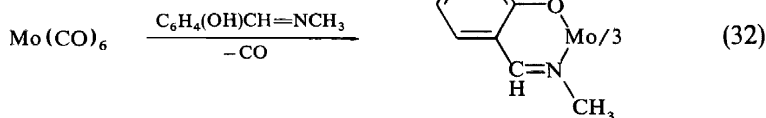
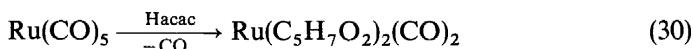
The i.r. spectra of the products obtained from reactions (28) and (29) suggest that the compounds have octahedral *cis* configuration, in agreement with earlier structural assignments for compounds of the same type^{77,78}. Since reactions (28) and (29) are very fast and substantially complete within the time of mixing, $[\text{ReBr}(\text{CO})_3\text{THF}]_2$ is a useful starting compound to obtain



disubstituted compounds of bromotricarbonylrhenium(i), which may be difficult to obtain otherwise. For $[\text{ReBr}(\text{CO})_3\text{THF}]_2$, ¹H n.m.r. measurements are possible because of its low-spin (diamagnetic) behaviour. Upon complexation with rhenium(i), the 2,5-hydrogens of the ring shift downfield by 0.73 ppm (with respect to uncoordinated tetrahydrofuran in the same solvent, CDCl₃) whereas the shift for the 3,4-hydrogens is smaller (0.33 ppm) and still in the same direction.

METAL CARBONYLS AS A SOURCE OF ZEROVALENT METALS

Some years ago we began to use metal carbonyls as starting materials for the synthesis of new organometallic and coordination compounds⁷⁹. For example, the following reactions were successfully carried out:



We have now found⁸⁰ that metal carbonyls of iron, cobalt and nickel can be used as starting materials for the synthesis of binary 9,10-phenanthrenequinone (PhQuinone) complexes. These are the first binary complexes of this

quinone to be reported in the literature. The reactions were the following (in tetrahydrofuran):



The reactivity of the metal carbonyls towards the quinone follows the usual pattern, i.e. based on qualitative observations, $\text{Ni}(\text{CO})_4 > \text{Co}_2(\text{CO})_8 > \text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$. The reaction with tetracarbonylnickel takes place at room temperature. The PhQuinone complexes of iron, cobalt and nickel are deeply-coloured solids (from green to black) slightly soluble in organic solvents, and thermally stable. The bonding is suggested to be through the oxygen atoms. This conclusion mainly arises from the infrared spectra. As

Table 8. C—O stretching vibrations (cm^{-1}) of coordinated and uncoordinated 9,10-phenanthrenequinone

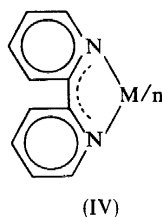
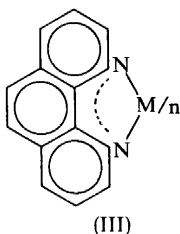
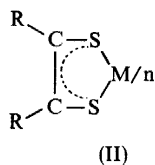
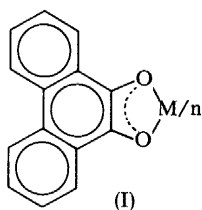
| | |
|---------------------------------|-----------------------------------|
| 9,10-Phenanthrenequinone | $\text{Fe}(\text{PhQuinoqe})_3$ |
| 1675 | 1460 |
| $\text{Co}(\text{PhQuinone})_2$ | $\text{Ni}(\text{PhQuinone})_2$ |
| 1460 | 1460 |
| | $\text{TiCl}_4(\text{PhQuinone})$ |
| | 1575 |

shown in Table 8, a strong band at 1460 cm^{-1} was attributed to the C—O stretching vibration of the coordinated ligand. This represents a shift of 215 cm^{-1} to lower wavenumbers with respect to uncoordinated quinone: this considerable shift is in favour of oxygen coordination and also suggests a considerable degree of electron transfer from the metal to quinone. This is confirmed by comparison with the data for the titanium compound, $\text{TiCl}_4(\text{PhQuinone})$. This compound, for which there is no question of electron transfer from the metal to the ligand, shows a wavenumber shift of about only 100 cm^{-1} with respect to uncoordinated quinone.

In these new *uncharged* phenanthrenequinone complexes of iron, cobalt and nickel, (I), the bonding can, therefore, be described in terms of σ -bonding to the metal and π -back-bonding to antibonding orbitals of the highly delocalized organic system. The bonding would then be similar to that existing in other more familiar complexes of transition metals with dithia-*ortho*-quinone,(II), heterocyclic diimines(1,10-phenanthroline),(III) and 2,2'-dipyridyl,(IV).

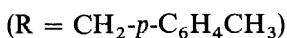
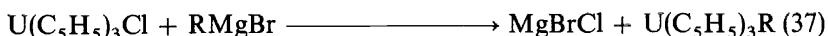
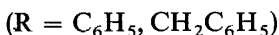
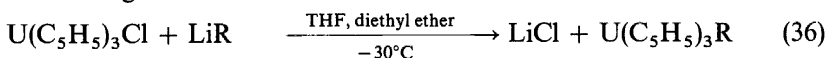
STABLE URANIUM-ALKYL AND URANIUM-ARYL BONDS

Since the discovery⁸¹ of bis(cyclooctatetraene)uranium in 1968, interest in organometallic derivatives of uranium has grown considerably. The x-ray structure of $\text{U}(\text{C}_8\text{H}_8)_2$ has shown⁸² that the molecule has a sandwich-type



of arrangement with eclipsed planar C_8H_8 rings giving the over-all D_{8h} symmetry.

Considerable progress in the field of organometallic chemistry of the actinides has been made recently with the preparation of the first alkyl and aryl derivatives of uranium(IV). This was achieved by Lugli, Brandi and Brunelli and their co-workers. A preliminary account of this work was reported at an international symposium⁸³. The compounds were obtained by the following reactions⁸⁴:



These compounds are moderately soluble in organic solvents and thermally stable in the solid state. The mass spectrum of the phenyl derivative showed the parent peak at m/e 510 and loss of a C_5H_6 fragment; since the same fragmentation was observed for $U(C_5H_5)_3C_6D_5$ it was concluded that a hydrogen transfer from cyclopentadienyl rings was involved in the formation of the C_5H_6 fragment. This is a further example of intramolecular hydrogen transfer from bonded cyclopentadienyl rings; some others have been discussed earlier when dealing with titanium-cyclopentadienyl derivatives.

Proton magnetic resonance shifts were measured for the compounds of reactions (36) and (37) and also for the methyl and n-butyl derivatives. The protons of α -alkyl groups (with respect to the metal) are characterized by very large chemical shifts, ranging from 194 ppm (from benzene at room temperature) for the α - CH_2 of $U(C_5H_5)_3(n-C_4H_9)$ to 213 ppm for the methylene group of $U(C_5H_5)_3CH_2C_6H_5$. The protons of the cyclopentadienyl groups are all in a narrow range of about 10 ppm. The magnetic resonance data are important because they establish these compounds, together with the chemical evidence available, as alkyl and aryl σ -bonded derivatives of uranium. An interpretation of these data will be useful for the theoretical

treatment of uranium-carbon bonds and for an insight into the problem of f-orbital participation to this bond.

ACKNOWLEDGMENT

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